Colloid Journal 2000 vol.62 N3, pages 380-385

Kinetics of crystallization of a flexible-chain polymer in pores

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Abstract

The kinetics of the isothermal crystallization of different fractions of poly(ethylene oxide) in cylindrical pores of a carbon adsorbent having a pore diameter of 480 A was investigated by the NMR relaxation method. Analysis of the isotherm shape and of the temperature dependence of the crystal growth rate showed that, for the polymer introduced into pores, the character of the primary nucleation and the crystallization regime are identical to those for bulk systems at the initial stage of the crystal growth. The change in the isotherm shape was attributed to the one-dimensional geometry of the growth, which was supported by the data on the character of the transverse magnetization decay in the melt. It was found that the dynamic degree of crystallinity attained upon completion of the process, P(c)(∞) depends on the crystallization temperature T(c): P(c)(∞) decreases with an increase in T(c). In the investigation of the subsequent melting of samples, it was found that a decrease in T(c) is attended with an increase of the fraction of the crystalline phase less ordered than lamellar crystallites. The transverse magnetization decay in amorphous regions during the crystallization was represented as a sum of two components; one of them was assigned to the crystalline phase. The population of this component was found to be proportional to the degree of crystallinity, whereas relaxation times of both components were independent of this parameter. | The kinetics of the isothermal crystallization of different fractions of poly(ethylene oxide) in cylindrical pores of a carbon adsorbent having a pore diameter of 480 angstrom was investigated by the NMR relaxation method. Analysis of the isotherm shape and of the temperature dependence of the crystal growth rate showed that, for the polymer introduced into pores, the character of the primary nucleation and the crystallization regime are identical to those for bulk systems at the initial stage of the crystal growth. The change in the isotherm shape was attributed to the one-dimensional geometry of the growth, which was supported by the data on the character of the transverse magnetization decay in the melt. It was found that the dynamic degree of crystallinity attained upon completion of the process, Pc(∞), depends on the crystallization temperature Tc: Pc(∞) decreases with an increase in Tc. In the investigation of the subsequent melting of samples, it was found that a decrease in Tc is attended with an increase of the fraction of the crystalline phase less ordered than lamellar crystallites. The transverse magnetization decay in amorphous regions during the crystallization was represented as a sum of two components; one of them was assigned to the crystalline phase. The population of this component was found to be proportional to the degree of crystallinity, whereas relaxation times of both components were independent of this parameter.